

## Answer to Referee #2

### Answer to general comments

Referee 2 addresses a number of comments relative to the development of the budget of carbon monoxide in surface seawater and mixed layer. His comments concern three main issues : CO sink and microbial consumption, the photochemical source and the gas transfer parameterization.

We should first point out that our goal in this paper was not to develop a precise and accurate model for CO production in the seawater, this is very far beyond our goal and our expertise. Very detailed budget for CO have been already proposed and described by Kettle, 2005; Fichot et al. 2010; Xie et al. 2009.

We would like only to present original results of simultaneous measurements of CO and NMHC in arctic waters and from very rough budgets and orders of magnitude, principally in the mixed layer establish or confirm: the photochemical origin of alkenes, the biological origin of isoprene, and the existence of a very minor process of biological production of CO so far observed only in laboratory experiments. These budgets are consistent with laboratory experiments conducted on phytoplankton species which show production rates normalized to the chlorophyll; moreover the average ratios of NMHC/CO in seawater are consistent with the order of magnitude of the respective quantum yields (AQY). In that sense, Table 5 presents only rough estimates, based on a weighted mean quantum yield.

Accurate budgets are not in the scope of this paper. We will improve the description of the CO production using accurate AQY proposed by the referee, but anyway, it will not be possible to use the same approach for alkenes; because accurate parameters are lacking. budgets of NMHC will still remain orders of magnitude.

Now concerning the estimation of the biological production of CO, we need to estimate the sinks in order to reach a budget in the column and derive from the content, the production. We agree that this can be more accurate, particularly; we will take into account the remark on the microbial consumption of CO and the deviation from the first order law, and the better parameterization of the piston velocity adapted to the experimental wind conditions.

We agree with referee2 that the NMHC consumption have been previously reported. However it is very uncertain to associate these processes with any parameterization since only the mechanisms have been described in details. Concerning the CO microbial consumption, it can be more precisely introduced in the calculations. On the basis of the remarks, i.e. first order decay for low concentrations, zero order for higher concentrations. However we can remark that nevertheless a first order consumption kinetics have been often used in the literature (Kettle, 2005 )

Concerning the parameterization of sea air exchanges, The Liss and Merlivat formula is based on data from a lake studies and wind tunnel and often considered as the lowest limit of the piston velocity. This is widely discussed in the paper of Nightingale et al. (2000)\* and others authors. The Wanninkhof et al parameterization is considered as an upper limit, we agree with this remark. The calculation in Table 5 is made for a wind of  $\sim 9\text{m/S}$ , and for the selected stations (Table6) often for wind conditions  $>5\text{ m. s}^{-1}$  they are in the range of values for which it is questionable to use one or the other parameterization. However, we will take into account the remarks and made more precise estimates of the piston velocity by choosing the best parameterization adapted to the corresponding wind and local situation (wind fetch, presence of ice pack, etc....).

\*Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J., and Upstill-Goddard, R. C.: In Situ Evaluation of Air-Sea Gas Exchange Parameterizations Using Novel Conservative and Volatile Tracers, *Global Biogeochem. Cy.*, 14, 373–387, 2000.

3. Yes we agree with this remark, but even if the CO variability results from a complex combination of various source and sink processes, simple correlations can sometime be observed as a result of a dominant process. The fact that no diurnal variability is observed does not mean however that the production process of CO is not driven by the radiation. This is only an observation; we can reduce the discussion in this paragraph and suppress the figure if needed.

4. We disagree with the referee's remark, according to his comments, our statement on a direct CO production by phytoplankton could be caused by false measurements or other artifacts. First owing to the precision of the measurements, deviations from a monotonic decreasing profile is a real effect, and we can not 'a priori' rule out artifacts. We are aware, that such CO production process is quite new and so far not really accepted by the scientific community. However, since we have a high experience in determining the production of trace gases (CO) from phytoplankton and given the fact, that this data are in the same range observed in laboratory studies (Gros et al. 2009) we are confident, that our assumption is valid. Other authors, highly experienced in CO measurements in the arctic also speculate about this production process from sea ice algae (Song et al. 2011).

Several tests of contamination have been performed on board including vertical profiles starting by samples collected in deeper layers (assuming to contain low or negligible CO concentrations) and comparison between sea surface samples collected from the pump on board, and surface samples collected with the 'Niskin bottles'. All these tests did not show any significant contamination however they have not been described in details in our paper.

If they were attributed to erratic CO contamination, deviations should appear at any depth, and be statistically distributed along the column, including 10 to 15 % of high values at the maximum depth (below 70 m.) which is not the case.

The argumentation of the referee concerns three points:

‘First, these subsurface maxima were mostly small irregularities. They occurred not only at or close to the chl-a maxima but also at other depths within the upper layer’.

We never claimed that this CO production process is of major importance. Since the observed small irregularities are in the range of phytoplankton CO production we determined previously in laboratory, we think that our conclusion is valid.

‘Second, they were not consistent, i.e. not all chlorophyll maxima having parallel CO maxima’.

Since the CO production is also very dependent on the various algae groups or even species as has also been described for other trace gases e.g. for DMS or isoprene, to us it is also clear, that not every chlorophyll maximum is accompanied by a CO maximum.

‘Third, there are a bunch of alternatives to explaining these CO peaks’:

All mentioned alternatives would require, that we occasionally did the mistake and sometimes not. Since we very carefully carried out all measurements and even present our small underestimation of the CO concentrations due to the time delay in the measurement we cannot follow the argumentation line of the reviewer which in itself carries some antagonism.

Concerning the possible role of particles we should point out that laboratory experiments as described by Gros et al. (2009) have clearly shown a production of CO by phytoplankton organisms under PAR radiations, which rules out the possibility of photo-production (UV induced) on particles.

5. Equation 6: in section 5.3. We have used here a weighted mean quantum yield as proposed by other authors for a simple approach (see Zhang et al., Environ. Sci. and Technol,40. 2006; and Xie et al. Limn. Oceanogr. 34. 2009). However we agree that AQY value determined in Arctic areas would be probably better. We will revise the calculations according to this remark. Once again even if we try to be more accurate for CO (we agree that one order of magnitude is easily reached if we are using wrong AQY) it will be impossible to produce a precise budget of NMHCs with the same degree of accuracy.

Answer to specific comments:

- 1 .OK we agree with this remark
2. Conrad et al. (1982) has been added in the references
3. We fully agree with this comment, the sentence must be changed.

4. We are aware that contamination or artifacts can be caused by any part of the sampling system, the equilibration cell of the analytical system. Concerning the water pump, it seems very difficult to check the status of the sampling system. We have performed simultaneous measurements from the water pump and from 'Niskin' bottles at the same depth. No significant difference was observed. A paragraph will be added for this discussion.

5. Samples storage was checked at station 68 on vertical profiles for which the CO at the surface was  $0.84 \text{ nmol L}^{-1}$  and at station 75 for surface samples with CO of  $2.1 \text{ nmol L}^{-1}$  over a time period of 9 hours.

6. For CO as well as for NMHCs, The discrete profiles were analyzed with the same flow segmentation method and the same cell as for surface water. We used 1 L samples, which allowed about height to ten measurements for CO (at a flow rate of 20 ml/min, a measurement for 5 minutes equal 100 ml per measurement).

7. 1 ml is the nominal volume. We are perfectly aware of this point, but the knowledge of the exact volume of each loop is not required. It can be avoided by a series of test consisting in measuring the standard alternatively in each loop (sample loop and standard loop) and calibrating the response in the sample loop with respect to the detector response in the standard loop. This has been done in the laboratory prior to the field experiment. The difference we observed was lower than 1%.

8. The column temperature was  $95^{\circ}\text{C}$ . This detail is added in the description of the technique.

9. Taking into account the experimental extraction efficiency for CO, and the analytical conditions and parameters (ratio of the flow rates or ratios of the volumes of the gas phase and water phase, extraction efficiency), 200 ppbv of CO in the gas phase corresponds to an initial CO concentration in seawater of about  $4 \text{ nmol L}^{-1}$  (\*). This falls perfectly in the range of the CO concentrations in seawater, except for relatively high CO value. Due to the linearity of the detector the calibration could be extrapolated to higher value.

Humidity in the sample does not produce interferences in the calibration, but a regular shift of the CO retention time toward shorter values. The column is periodically regenerated for this reason. For NMHC, the humidity is removed by using a permapure system (Nafion dryer) and a magnesium perchlorate trap.

(\*) The major part of CO initially in the water phase is transferred by equilibration to the gas phase, one should therefore consider that the initial content of CO in seawater is the number of moles remaining in the water phase at the equilibrium (theoretically given by using the Henry's law), plus the number of moles transferred into the gas phase; experimentally it is given by the number of moles in the gas phase divided by the experimental extraction efficiency (here 56% for CO). The volumes of the respective phases

in contact (water, gas) and the extraction efficiency, which depends on the solubility of CO or on its Henry's law constant, are the basic parameters to take into account.

(See also answer to referee 3 concerning this point).

10. We agree to give the blanks levels.

11. We gave a detailed description of the pigment measurement and used the following references in the text. Since all references are listed in the reference list, we are uncertain what is missing.

Listed References: Barlow et al. (1997), Bidigare (1991) and Jeffrey et al. (1997), Mackey et al., 1996

12. All measurements were carried out in the framework of the DSHIP data acquisition system. The data are sampled every second as non-validated raw-data in physical units. The following information is available on the following web site:

[http://www.awi.de/de/infrastruktur/schiffe/polarstern/bordwetterwarte/continuous\\_measurements/sensor\\_information/](http://www.awi.de/de/infrastruktur/schiffe/polarstern/bordwetterwarte/continuous_measurements/sensor_information/)

Wind direction and wind speed are measured at a height of 37m above sea level at the port and starboard side of the ship. Only the windward sensor gets registered.

Global radiation is measured by using an artificially ventilated pyranometer. A description of the instrument can be found at:

<http://www.kippzonen.com/product/cm11.html>.

13. The Sensor is a Cyclops-7 by Turner Design (USA) equipped with a CDOM/FDOM sensor, Excitation wave length: 325nm, Emission wave length 425 nm, and is integrated in a ferry box system, continuously monitoring data from the surface water (6m) The entire instrument provides a self-cleaning every day and is maintained by the technicians on board R/V Polarstern. Usually no drift has been observed for this instrument. In general it would be possible to transfer the relative units into a range between 0 - 20 ppb Quinine Sulfate, however, it will still be relative units and goes beyond the scope of this paper.

14. We are aware of this underestimation. However the used sensor was not optimal to determine UVA since the results below 350nm are highly questionable. We therefore were able to only present data between 350 and 400 nm.

15. Minimum value observed during at least a relatively long period (24 H) during the experiment

16. Both terms are used in the literature; however we agree that the term Henry's law constant is more frequently used.

17. They are defined by the bathymetry and salinity

18. We agree with this remark.

19. Yes the samples were performed in partially ice covered waters not in the ice itself.

20. This is an observation (in the section results) this fate has not to be discussed here. It is probably an indirect effect due to changes in CDOM (see section 4).

21. Obviously, but owing to the assumed kinetics of production, diffusion and destruction processes involved, the production term drives the profile shape.

22. We agree with this remark.

23. We definitely take into account this relevant remark, owing to the experience of the referee in this domain.

24. The NMHC consumption was determined on duplicates with the same procedure as for CO. Samples were stored at 0°C and analyzed by GC within a time delay extending to several hours.

25. A detailed table will be produced.

26.  $C_{ML}$  Bar was calculated obviously as the depth weighted mean, arithmetic mean has not great significance.

27. We take into account this relevant remark and should present at least budgets or averaged budgets in various water masses.

28. Our remark concerns the budgets below the mixed layer. The idea is very simple and obvious: a budget cannot be established if the sinks are highly uncertain or poorly parameterized, this is particularly the case for NMHC's. In the mixed layer the budget can be approximately approached since the major sink seems to be the ventilation to the atmosphere. This is exactly what we have proposed to do.

29. As CO decreases exponentially, (see also point #37) we have  $CO_z = CO_{surface} e^{-\lambda z}$ , hence the integral of CO concentration from  $z=0$  to  $Z$ =mixed layer depth is calculated. On the averaged profile we have:  $\lambda = 8.2 \cdot 10^{-2} m^{-1}$  and  $Z_{ML} = 20$  m.

$$\overline{CO_{ML}} = \frac{1}{Z_{ML}} \int_0^{Z_{ML}} C_{(z=0)} e^{-\lambda z} dz \approx 0.49 CO_{(z=0)}$$

We don't understand here what means the referee's comment and what is the real question. This seems obvious: the exponential law being a monotonic decreasing function, the average value over one interval is comprised between the values at the two limits of this

interval, which means that the average CO is comprised between CO at the surface and CO at  $z=20\text{m}$ .

30. We agree with this remark.

31. We agree with this remark, the sink effect will be included in the discussion.

32. We agree with this comment, we will remove this sentence.

33. Yes we agree, we are using CO AQY for arctic seawater as proposed.

34.35. We fully agree with these remarks, Fichot's model presents the photoproduction, i.e. the source distribution and not the CO distribution with depth which can include transport by diffusion. We reconsider our argumentation owing to this important point of the discussion. However even if the transport from surface layers or mixed layer to deeper layers, as pointed out by the referee, can lead to significant concentrations in depth it can not explain a secondary maximum as it is sometimes observed; this is simply physically irrelevant, the existence of an increase in depth can be only produced by an 'in situ' production either by physico-chemical or biological processes.

36. Not necessary but it is in favour of same mechanisms.

37. Quasi exponential means that the CO profile with depth can be described by the linear relationship with a high degree of determination ( $R^2 > 0.9$ ):

$$\ln(\text{CO}_z / \text{CO}_{z=0}) = -\lambda z$$

We don't understand the referee's remark. There is no better mathematic equation, deviations from this law are a matter of statistics and uncertainty in the measurements. In the same way, there is no better mathematic equation to describe a quasi linear relationship than an affine function.

Many authors consider that in a first approach the UV penetration in the surface waters follow an exponential law (Kettle 2005; Fichot et al. 2010) with a  $K_d$  coefficient, this is also what we experimentally observed here on the UV profile. Furthermore, all our profiles of CO

can be fitted by an exponential law, at least down to 50m. depth with a high coefficient of determination (  $R^2 > 0.8$  ), this is purely experimental. This ascertains also the fact that deviation from a first order law for the CO decay can be probably of secondary importance.

38. We agree, graphs will be added to compare the experimental profiles and the deviation with fitted profiles.

39. In a range of 300 to 400 nm. Riemer shows a large range of AQY, this is why it is highly uncertain to use their data but they are the only quantum yields to our knowledge published for NMHCs photoproduction.

40 We fully agree with this very relevant remark. This figure can be removed from the discussion.

41. Chlorophyll data will be added to the figures.